Colloidal Coal Hydroliquefaction
Catalyst Preparation

Diane R. Milburn, Bruce D. Adkins[*], and Burtron H. Davis

Center for Applied Energy Research
3572 Iron Works Pike
Lexington, KY   40511

[*]Akzo Chemicals, Inc.
13000 Bay Park Road
Pasadena, TX   77507

Introduction

Typical hydrotreating catalysts, consisting of Mo and W or Ni on aluminoxide, are pelletized and added to and withdrawn from the reactor in batches. The effects of diffusivity on the global reaction rate as well as on dispersion of the active metals are poorly understood.

Current research efforts aimed at cost reduction include dispersion of "disposable" unsupported metals in the feed streams (ref. 1) and impregnation of high surface aerogel supports (ref 2). In the standard incipient wetness impregnation a strongly bridging solvent such as water is used to dissolve the metal salt precursor. On drying, the support is compacted and pore structure of the final product may bear little resemblance to the original starting material. This study involves utilization of commercial colloidally sized aluminum supports to prepare a homologous series of catalysts to study the effects of solvent and solvent removal on structure of the support and on dispersion of the active phase.

Experimental

Four impregnation techniques utilizing Degussa Aluminoxide-C (fumed process, 150-200 Å discrete spherical particles) and ammonium molybdate from Fisher Scientific Co. (83% MoO_3) are described below.

Incipient Wetness, (IW)

The Mo salt is dissolved in distilled water and added dropwise to the support. This continues until the support is at "incipient wetness", i.e. the point where unbound moisture is about to become available. The catalyst is dried at ca. 120°C for 12 to 24 hours,

ground with a mortar and pestle and calcined at 500°C for 4 to 6 hours.

Ethanol Slurry, Vacuum Dried, (EtOH-V)
The salt is dissolved in excess ethanol and a slurry is made by adding the support material. The mixture is stirred for several hours and then placed in a vacuum oven at ca. 100°C for 36 to 48 hours. This is followed by grinding as described above.

Ethanol Slurry, Rotary Evaporated, (EtOH-R)
Identical to EtOH-V except that solvent removal is achieved in a rotary evaporating apparatus over a period of 4 to 6 hours.

Critical Point Solvent Evaporation, (CPSE)
A slurry of is made of metal salt, solvent and support material as described for EtOH-V. The slurry is maintained under an inert gas pressure which is higher than the vapor pressure of the solvent at a temperature slightly lower than the critical temperature; the slurry is then heated above the critical point. A very rapid evaporation of the solvent occurs at the critical point (on the order of minutes or less). The catalyst is then removed and calcined as above.

Scanning Electron Microscopy was performed on the samples to observe gross differences in physical structure. The instrument used was an ETEC Omniscan SEM equipped with a PGT-1000 data acquisition and analysis system. Pore structure and surface area measurements were calculated from nitrogen adsorption/desorption isotherms made on a Digisorb 2500 instrument and from combining Hg penetration scans made at three pressure ranges on a Quantachrome Autoscan Porosimeter.

Catalyst Structure

Physical characteristics for five catalysts prepared by the methods described above, for fresh Al$_2$O$_3$, and for Al$_2$O$_3$ which has been wetted and dried as described for the IW sample are summarized in Table 1. The data show that the tap density (determined by measuring the volume of a known weight of material which had been gently tapped in a graduated cylinder) increases significantly in all treatments of the support material except for the case of the CPSE preparation. SEM micrographs indicate that the IW, EtOH-V, and EtOH-R processes yield irregularly shaped particles with a wide distribution of sizes as is typical for a grinding process. In contrast, the sample prepared using the CPSE process is composed of secondary particles which are much more uniform in size and shape.

The BET surface area of Al$_2$O$_3$ increases when wetted and dried. This is due primarily to the large numbers of interparticle contacts formed during drying; condensation around

an interparticle contact zone essentially adds a contribution to the isotherm volume. Figure 1 shows the comparison of pore volumes calculated from the nitrogen adsorption isotherms for these catalyst samples with fresh Degussa aluminoxide-C. The CPSE most closely resembles the fresh support material (shown by the dotted line), the wetted alumina and the IW sample show the greatest increase, and the EtOH-V and EtOH-R samples are intermediate in calculated volume increase from fresh Al_2O_3. The mercury porosimetry data for total pore volume indicates that decreasing the severity of compaction during catalyst preparation, either by lowering the bridging strength of the solvent or by increasing the rate of solvent removal, results in an increase in pore volume.

Active Phase Dispersion

It is known that the selectivity for octenes in the catalytic dehydration of octanol is a function of the acid/base properties of the catalyst used (ref. 3). This reaction has been used in measuring the dispersion of MoO_3 on alumina (ref. 4). The selectivity, at constant conversion, for our series of catalysts, for pure MoO_3 and for pure γ-Al_2O_3 is shown in figure 2; the line represents selectivity for a series of IW catalysts with increasing MoO_3 loadings. These data indicate that dispersion of the active phase decreases in the order:

$$IW > EtOH-V > EtOH-R > CPSE.$$
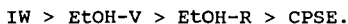
X-Ray diffraction scans suggest that both the IW and CPSE contain little or no crystalline MoO_3.

Hydrogenolysis Performance

Hydrogenolysis of 1,3,5-trimethylbenzene (tmb) in a plug-flow reactor was used to compare activity for the series of catalysts (ref 5). The catalysts were diluted with an inert α-Al_2O_3 (Fisher Scientific, $0.96m^2/g$) to minimize the effects of physical differences in the test catalysts by making the reactor beds similar in density, volume and particle size. The catalyst was first reduced in flowing H_2 overnight at 450^oC; the reaction mixture was a 10:1 molar mixture of H_2 and 1,3,5-trimethylbenzene.

For the IW catalyst, hydrogenolysis of 1,3,5-tmb to m-xylene was the dominant reaction; equilibrium between the two had been reached at residence times of 15 minutes. Small amounts of o- and p-xylene as well as 1,2,3- and 1,2,4-tmb were also detected. The EtOH-V and CPSE showed the same product selectivity, although concentrations are shifted downward and the equilibrium between m-xylene and 1,3,5-tmb was not reached until residence times of approximately 1 hour.

The greatest tendency toward hydrogenolysis was seen for the 17% MoO_3 catalyst. The equilibrium between 1,3,5-tmb and m-

xylene is already established at residence times of 15 minutes, but at longer times the m-xylene production declines and a corresponding increase in benzene and methane is observed. TEM micrographs revealed large MoO_3 crystallites on the 17% MoO_3 sample not seen in any of the 12% loading samples. XPS analyses on the two EtOH-V catalysts show the presence of a peak for a more reduced species of Mo in the 17% loading not present in the 12% catalyst reduced under the same conditions. These data suggest that the Mo in excess of one monolayer is apparently more reduced than the supported Mo.

Conclusions

Choice of solvent and method of solvent removal are critical factors in determining the final structure of a supported catalyst. The use of a less polar solvent and subsequent rapid removal is shown to minimize compaction of the colloidal alumina particles. However, greater metal dispersion and higher hydrogenolysis activity is indicated for catalysts prepared using water. Further investigation is needed to determine the effects of subsequent impregnation, and coimpregnation, of promotors, as well as the removal of water at it's critical point.

References

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Table 1.
Physical Properties

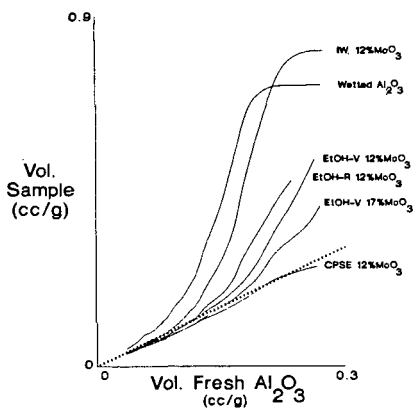|	Tap Density (g/cc)	BET Surface Area (m2/g) Corrected for Mo	Total Pore Volume (cc/g) Mercury Penetration
Fresh Aluminoxide	0.07	98.32	3.88
Wetted Aluminoxide	0.70	117.39	0.89
IW 12% MoO_3	0.56	111.01	1.33
EtOH-V 12% MoO_3	0.34	110.73	2.60
EtOH-V 17% MoO_3	-	126.01	-
EtOH-R 12% MoO_3	0.29	108.03	2.17
CPSE 11% MoO_3	0.05	102.88	7.33

Figure 1. Comparison of pore volumes calculated from nitrogen adsorption isotherms for this catalyst series with fresh Degussa Aluminoxide-C.
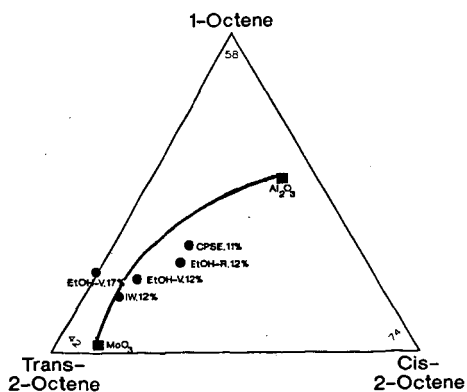

Figure 2. Product selectivity of the dehydration of octanol for pure Al_2O_3 and MoO_3, a series of MoO_3/Al_2O_3 catalysts prepared by incipient wetness (-), and the series of MoO_3/Al_2O_3 prepared for this study (●).